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13. ABSTRACT *(Maximum 200 words)*

First-principles density-functional methods using LAPW and LAPW linear response method were applied to study the incipient ferroelectric $SrTiO_3$. Despite similarities to $BaTiO_3$, $SrTiO_3$ remains paraelectric down to zero temperature, transforming instead to an antiferrodistortive structure at 105 K. As a function of wavevector, the linear response calculations show structural instabilities along the R-M-R line in the Brillouin zone, consistent with this antiferrodistortive ground state. Although a ferroelectric-type instability was also found near the zone center as in $BaTiO_3$, the phase space of this instability is greatly reduced by comparison. Moreover, we find that the antiferrodistortive phase is stable, marginally, against ferroelectric structural distortions. In combination, these findings help explain the absence of a transition to a ferroelectric structure.

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A. Description and Motivation of the Scientific Research Goals

Although it possesses the same high-temperature cubic perovskite structure as ferroelectric materials like $BaTiO_3$ and $KNbO_3$, $SrTiO_3$ exhibits qualitatively different temperature-dependent behavior. It transforms to a non-ferroelectric phase when the temperature is lowered below $T_c = 105$ K, due to a soft-mode antiferrodistortive (AFD) instability at the R-point, the Brillouin zone-corner. The atomic motions in this AFD mode are characterized by rotations of the TiO_6 octahedra about a [1 0 0] axis. Below T_c, these octahedra are slightly rotated, with the twist angle about the tetragonal c-axis being the order parameter of the transition. Upon further cooling, the dielectric constant rises in a Curie-Weiss manner until about T = 35 K, where it continues to increase, but in a non-singular manner, and at T = 3 K and below, it saturates to a value of about 10^4, but a further structural phase transition does not occur. Due to these unusual properties at low temperature, $SrTiO_3$ has been subjected to extensive studies in the past few decades. In recent years, first-principles density functional theory calculations using the local density approximation (LDA) have achieved remarkable success in determining the physical properties of ferroelectrics, including the equilibrium atomic configurations, lattice vibrational frequencies, and the underlying microscopic mechanisms behind macroscopic behaviors. For instance, our recent first-principles linear response calculations for $KNbO_3$ revealed large planar regions of phonon instabilities in the Brillouin zone. These correspond, in real space, to chains along the [1 0 0] directions of atoms coherently displaced along the chain direction. Subsequent molecular-dynamics simulations of $KNbO_3$ have shown that these chains are dynamic rather than static and that they are preformed even in the high-temperature paraelectric phase. [2] (Note: references in square brackets refer to publications in Section D.) Motivated by this success, we undertook a first-principles study of $SrTiO_3$ in both cubic and AFD phases to examine the nature of its structural instabilities to explain the its distinctive properties.

B. Significant Results

Comparing with experimental phonon frequencies obtained with neutron scattering and infrared spectroscopy at high symmetry points in the Brillouin zone, the theoretical phonon frequencies are found to be in good agreement. [1, 3] In addition, we correctly obtain the known instability at the R-point in the Brillouin zone (BZ), which is responsible for the AFD phase transition at 105 K. Moreover, we found that the AFD instability extends along the entire R-M-R line in the BZ, forming a one-dimensional cylindrical tube in the BZ. We also found that this instability competes with a ferroelectric instability centered at q = 0, whose phase space is considerably reduced compared to $BaTiO_3$ and $KNbO_3$. Total energy calculations of the AFD instability showed that decreasing the volume enhances the AFD instability, increasing the corresponding double-well depth. The angle characterizing the TiO_6 octahedral rotations was found to be about a factor of three larger than observed, however. This is in agreement with an earlier LAPW calculation, and after extensive tests, we ascribed this quantitative discrepancy to the limitations of the local density approximation. [3]

Even though no further phase transition is observed at low temperatures, the sharp rise in the dielectric constant suggests the possibility of a FE instability that may be suppressed by the

zero-point motion of the atoms. Such an instability should be revealed by computing the full zone-center dynamical matrix of the AFD structure (10 atoms per unit cell). We focused on investigating the influence of the AFD transition on the ferroelectric instability of the Γ_{15} (with respect to the cubic structure) ferroelectric mode. We imposed the calculated Γ_{15} mode eigenvector distortion along both the c-axis and a-axis in the AFD unit cell (the TiO_6 octahedral rotations are about the c-axis), and setting the twist angle of the TiO_6 octahedra at the 1.4^o value measured at 105 K. We found that the AFD structure is stable, marginally, against the imposed distortions. [3] Thus large ferroelectric-like fluctuations might be expected in the AFD structure, leading to the increase of the dielectric function. Since the AFD structure is stable, however, with respect to the ferroelectric Γ_{15} distortions, the crystal never actually transforms to a ferroelectric phase.

C. Impact of this Work on Future Research

We have shown that while the AFD structure is stable against subsequent ferroelectric distortions, it is only marginally so. Thus ferroelectric-like fluctuations might be expected even at low temperatures, resulting in the observed large dielectric function. It is likely that future work would therefore focus on these fluctuations.

D. List of Publications/Reports/Presentations Under This Grant

Papers Published in Refereed Journals

[1] "*Ab Initio* Linear Response Study of $SrTiO_3$," C. LaSota, C.-Z. Wang, R. Yu, and H. Krakauer, *Ferroelectrics* **194**, 109 (1997).

[2] "Precursor Structures in Ferroelectrics from First-Principles Calculations," H. Krakauer, R. Yu, C.-Z. Wang, and C. LaSota, *Ferroelectric*, in press, available in electronic form at Los Alamos National Laboratory physics e-print archive at http://xxx.lanl.gov/abs/cond-mat/9710088.

[3] "First-Principles Study of $SrTiO_3$ in Cubic and Tetragonal Phases," C. LaSota, C.-Z. Wang, R. Yu, and H. Krakauer, in press.

Presentations - Invited

[1] *4th Williamsburg Workshop on First-Principles Calculations for Ferroelectrics*, Feb. 4-7, 1996, Williamsburg, VA. *Ab Initio* Linear Response Study of $SrTiO_3$, C. LaSota, C. Z. Wang, R. Yu, and H. Krakauer.

[2] *Williamsburg Workshop on Ferroelectrics*, Feb. 2-5, 1997, Williamsburg, VA. H. Krakauer, R. Yu, C.-Z. Wang, and C. LaSota.

E. Participants and Status

Henry Krakauer - PI, Professor of Physics

Christopher LaSota Graduate Student [supported by this grant], Ph.D. expected 1998.